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CHARACTERISTICS OF META-DINITROBENZENE DRY CELLS

by

James Bruce Doe

January 1969

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TECHNICAL REPORT ECOM-3089

CHARACTERISTICS OF m-DINITROBENZENE (m-DNB) DRY CELLS

by

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FORT MONMOUTH, NEW JERSEY

ABSTRACT

The performance of the $Mg/Mg(ClO_4)_2$/m-DNB system is evaluated for various temperatures, hourly rates, and shelf-life periods. Extensive data is given for three cell sizes: "R(N)", "A" and "D". Techniques for fabrication of the above cells, which are adaptable for high-speed assembly, are mentioned. Finally, a comparison of the $Mg/Mg(ClO_4)_2$/m-DNB system with the $Mg/Mg(ClO_4)_2/MnO_2$ is given with respect to energy densities and performance curves. Improvements in cathode efficiency, corrosion inhibition, and a mechanical seal will have to be initiated in the Mg/m-DNB system before it will be able to compete with the present Mg/MnO_2 system.

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CHARACTERISTICS OF m-DINITROBENZENE (m-DNB) DRY CELLS

INTRODUCTION

The object of this report is to present the evaluation and test results of the $Mg/Mg(ClO_4)_2$/m-DNB dry cells produced by Bright Star Industries, Inc. under USAECOM Contract DA28-043-AMC-01401(E).[1] The fabrication of these cells incorporated optimum techniques that are readily translatable to methods of high-speed fabrication of $Mg/Mg(ClO_4)_2$/m-DNB dry cells in the "R(N)", "A", and "D" sizes. The "R(N)" notation designates a magnesium can of "R" diameter and "N" height. This type of can configuration provides sufficient magnesium for the electrochemical reaction with m-DNB whereas the standard "N" can does not. All other cell size notations are standard. A comparison of the $Mg/Mg(ClO_4)_2/MnO_2$ system with the $Mg/Mg(ClO_4)_2$/m-DNB scheme will be given with respect to hours of service, watt-hours per pound, and watt-hours per cubic inch. Earlier work on the $Mg/Mg(ClO_4)_2$/m-DNB system was reported by Pawlak[2,3], Murphy and Wood[4], and Doe and Wood[5].

CELL STRUCTURE

The basic electrochemical cell system incorporates an AZ21 magnesium alloy can as the anode and negative terminal and a carbon rod as the positive terminal and current collector which is surrounded by the cathode mix or depolarizer. This mix is composed of the components listed in Table 1.

TABLE 1

CATHODE OR DEPOLARIZER MIX

FUNCTION	CONSTITUENT	WEIGHT - %
Current Collector	Carbon Black (United XC6310-4)	32.4
Depolarizer	m-Dinitrobenzene (m-DNB) (Containing 17% Water)	64.8
Corrosion Inhibitor	Barium Chromate	2.8
Electrolyte	1.25M Magnesium Perchlorate ($Mg(ClO_4)_2$) Containing 0.2 gm/Liter Lithium Chromate (Corrosion Inhibitor)	2 ml/gm m-DNB

The cathode mix is prepared in a Patterson-Kelley twin-shell blender (liquid-solids type, with intensifier), and the complete mixing details are given in Reference 1. This cathode mix provides a cell which is comparable in performance to that made by special "hand" techniques.[2]

The cathode mix and the anode(Mg) are separated by a microporous barrier material (uncoated salt-free Kraft paper liner-0.035-inch thick) which is permeable to the flow of ions, and tends to prevent the migration of insoluble structural or waste products between the cathode mix and the magnesium can. At the bottom of the magnesium can, there is a paper disk ("bottom washer") made of saturating Kraft paper-0.0115-inch thick which acts as an insulator or separator between the magnesium can and the cathode mix.

A carbon rod (Speer Oiled) is inserted in the cathode mix or bobbin to act as a current collector. A brass cap with a vent hole (0.014-inch diameter) is placed on the electrically conducting but chemically inert carbon rod to aid in making electrical contact and to act as a dispersal point for reactant gases. Prior treatment (oil) of the carbon rod enables it to be porous enough to permit the escape of hydrogen produced in the cell especially at the low hourly discharge rates, while at the same time not permitting the escape of electrolyte or water vapor. Since the escape of hydrogen must be allowed, i.e., the cell cannot be hermetically sealed, a seal, such as Mitchell Rand Wax (1850 EX), is employed which minimizes air access and moisture loss by evaporation to increase the shelf life. Support for this seal is given by the seal washer which is made of paraffin-impregnated Kraft board (Tuf Board)-0.038-inch thick. The cells can be sealed immediately with no aging required. Some air space is left between the cathode mix and the seal to provide for expansion of cell ingredients. A mix-washer (saturating Kraft paper-0.0115 inch thick) serves to keep the ejection plunger clean during the bobbin extrusion operation. The assembly of the above cell is accomplished by standard bobbin extrusion and consolidation machines and is well adapted to the mass production procedures of today. Typical cell dimensions and weights are presented in Table 2.

TABLE 2

DIMENSIONS AND WEIGHT OF CELL COMPONENTS

CHARACTERISTICS	CELL SIZE		
	R(N)	A	D
Overall Height (inches)	1.063	1.875	2.250
Inside Diameter (inches)	0.416	0.547	1.098
Can Wall Thickness (inches)	0.040	0.040	0.075
Can Weight (gms)	2.001	4.366	18.880
Cell Weight (gms)	4.676	13.060	58.940
Bobbin Weight (gms)	1.805	6.420	31.[illegible]80

A cross-section of a typical $Mg/Mg(ClO_4)_2$/m-DNB dry cell is shown in Figure 1.

DISCHARGE DATA

From Figures 2 to 13, it is evident that the $Mg/Mg(ClO_4)_2$/m-DNB cell discharge curve is flat over a fairly long service period from 0°F. to 70°F. except for the rates below four (4) hours. This flat portion of the discharge curve is advantageous in that it is sort of a battery-induced "voltage regulation" up to just before the end-voltage (0.9 volt/cell). This is desirable in equipment requiring minimal voltage fluctuations. From these curves, it is obvious that as the temperature decreases so does the service life to 0.9 volt/cell. The $Mg/Mg(ClO_4)_2$/m-DNB system is much more sensitive to temperature of operation than the $Mg/Mg(ClO_4)_2/MnO_2$ system. Details concerning these temperature effects are given in the discussion on System Comparisons.

There is some initial delay time (0.3 seconds average at 70°F.) experienced in initiating fresh cells under continuous discharge. At temperatures below 70°F., the delay increases to several minutes. A battery stored for 26 weeks at 113°F. has an initial delay of 15 seconds under a continuous discharge. This may be a function of H_2O loss caused by the type of seal employed, and additional information will be required for a cell to reach operating voltage (in this case, 0.9 volt/cell or greater) after the circuit is closed. The delay time as used above is the time for a cell to reach operating voltage, i.e., 0.9 volt/cell or greater. Further development will be undertaken to evaluate the intermittent and storage effects on delay time.

TEMPERATURE EFFECTS

The curves presented in Figures 14 to 18 were obtained on fresh cells and indicate that $Mg/Mg(ClO_4)_2$/m-DNB cells employing 1.25 M $Mg(ClO_4)_2$ electrolyte are highly dependent upon operating temperature below 70°F. Generally, the most service life from these cells is obtained in the temperature range between 70-113°F. It is to be noted that these curves are a partial summary of the data presented in the discharge curve discussion.

SHELF LIFE

Based on cell groups, the storage at 70°F. has the least degradation of the initial capacity as compared to storage at 113°F. and 130°F. In Tables 3 to 5, shelf life data are presented for the "R(N)", "A", and "D" size cells at various temperatures and resistances for a specified storage period.

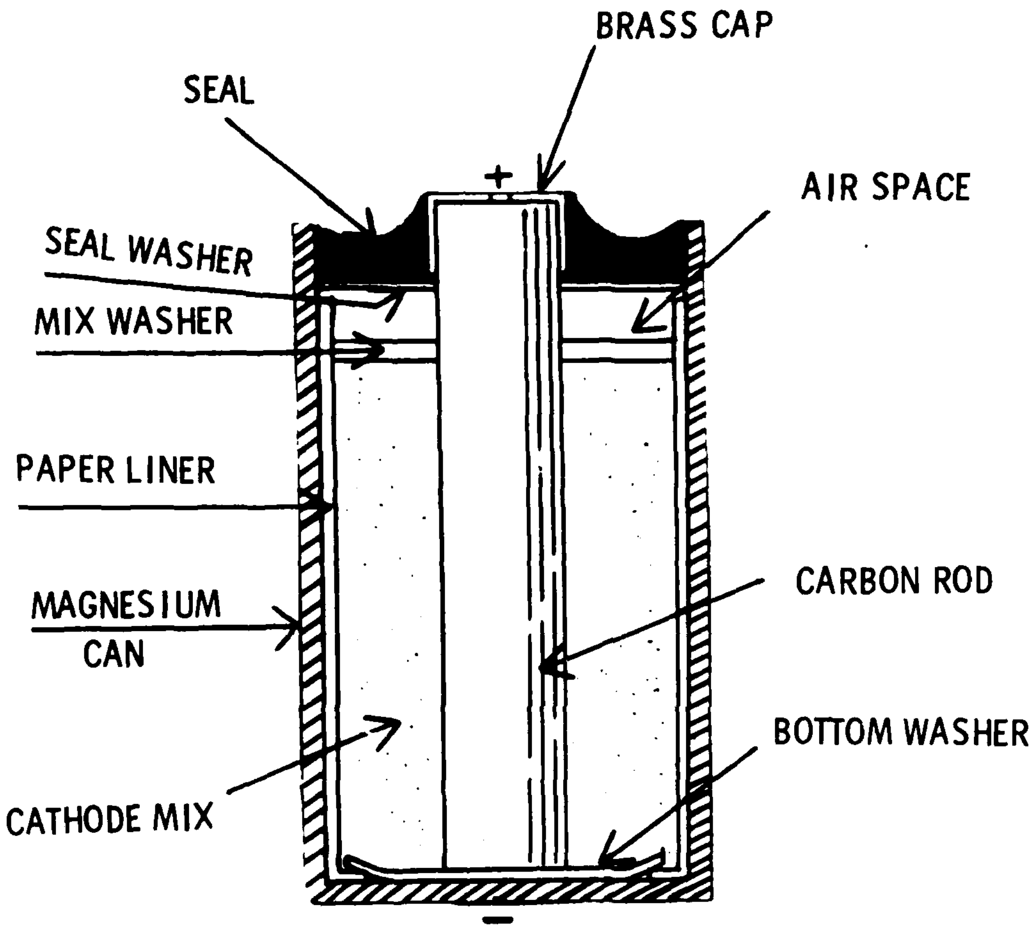


FIGURE 1. CROSS-SECTION VIEW $Mg/Mg(ClO_4)_2$/m-DNB DRY CELL

DISCHARGE CURVES AT 70°F FOR "R(N)" CELLS

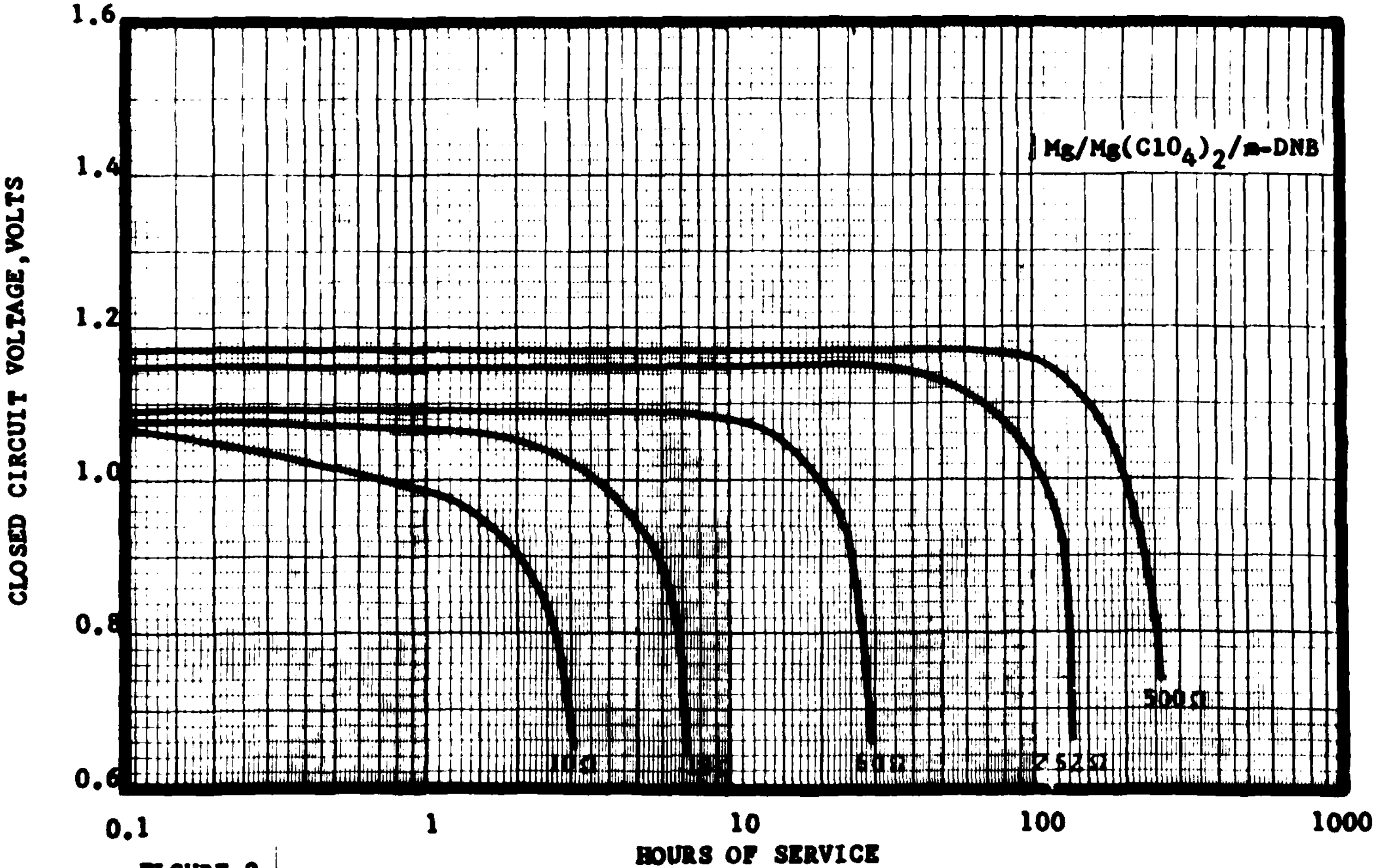


FIGURE 2

DISCHARGE CURVES AT 40°F FOR "R(N)" CELLS

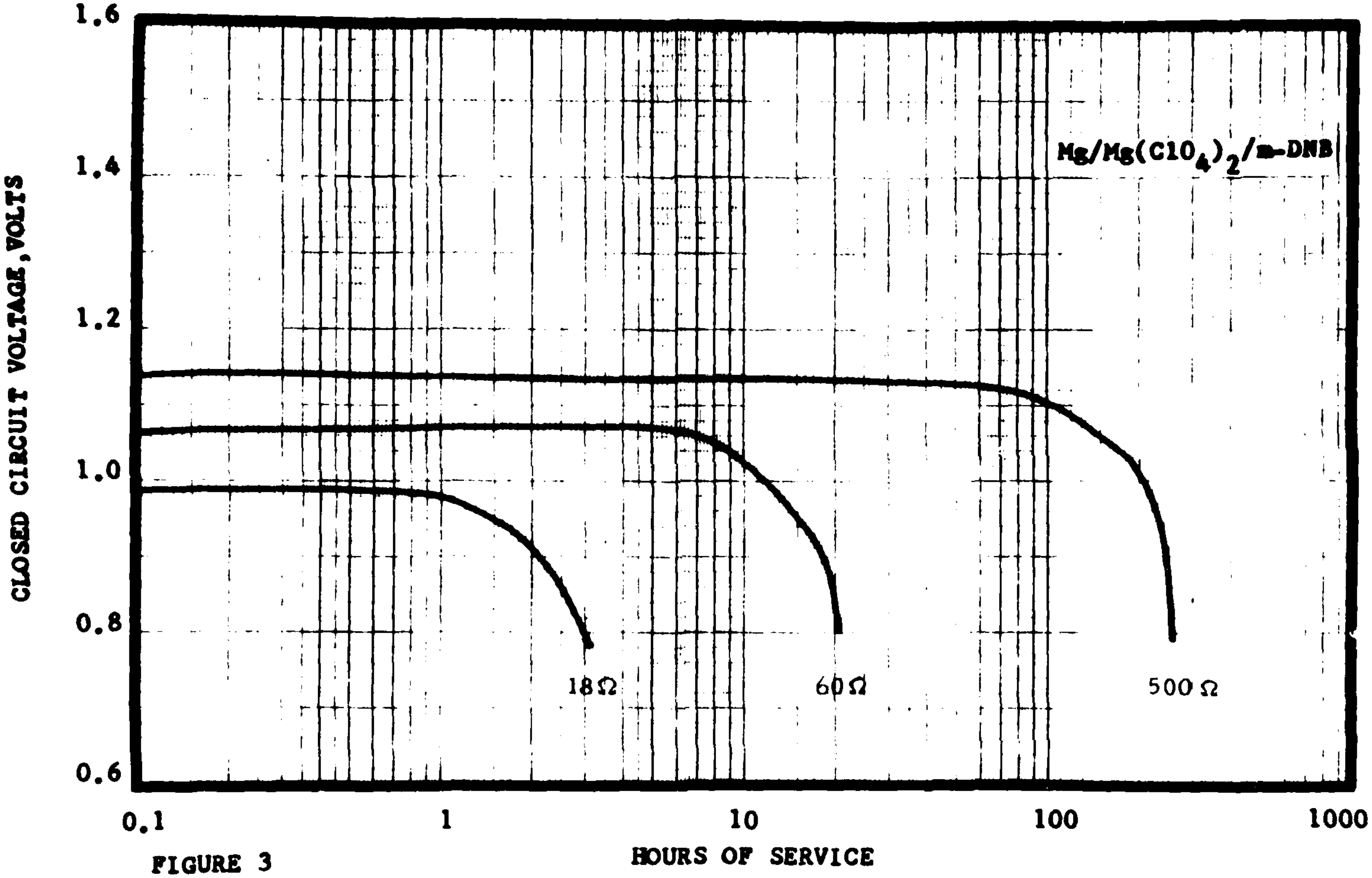


FIGURE 3

DISCHARGE CURVES AT 20°F FOR "R(N)" CELLS

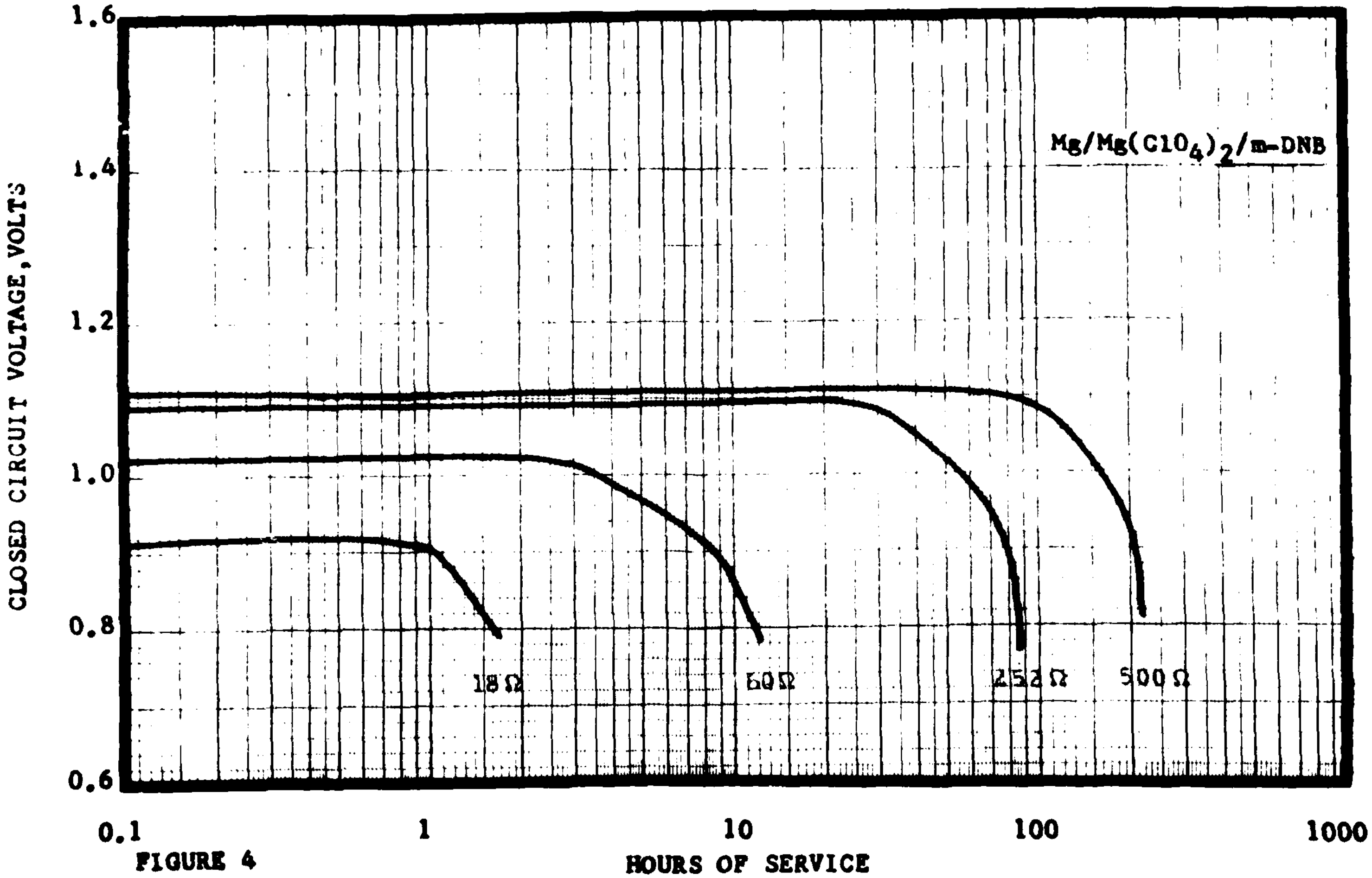


FIGURE 4

DISCHARGE CURVES AT $0^{o}F$ FOR "R(N)" CELLS

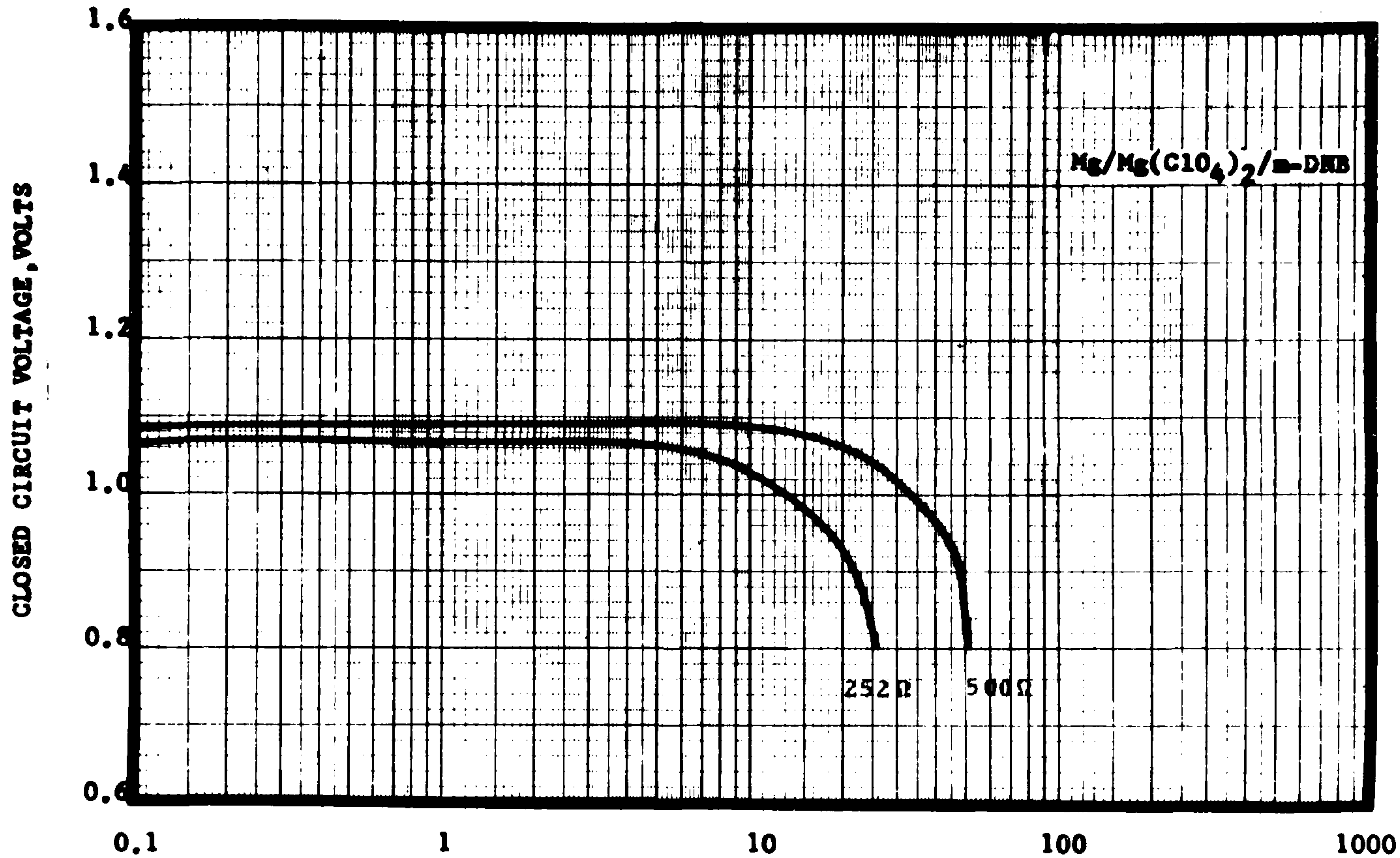


FIGURE 5

DISCHARGE CURVES AT 70°F FOR "A" CELLS

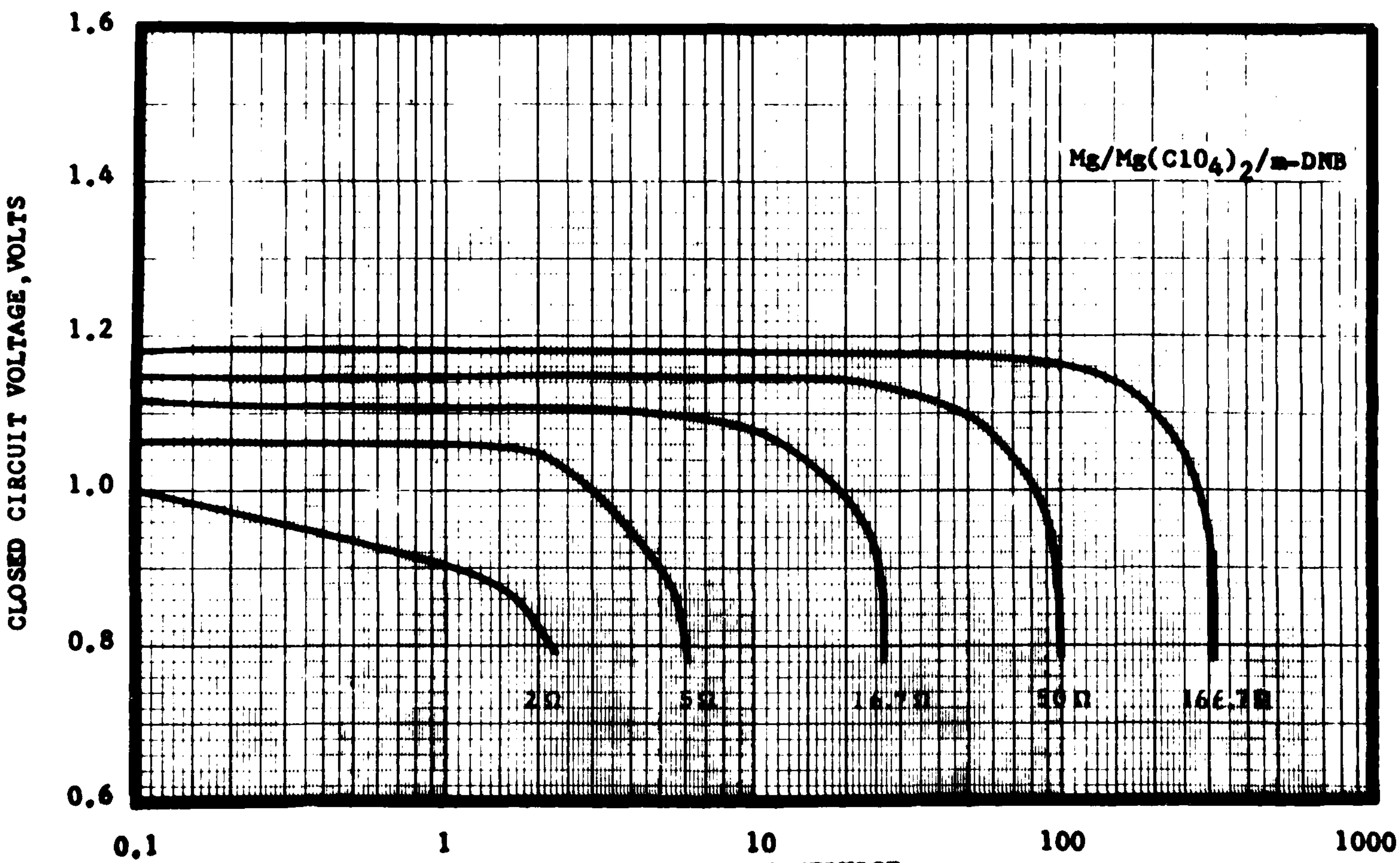


FIGURE 6

DISCHARGE CURVES AT 40°F FOR "A" CELLS

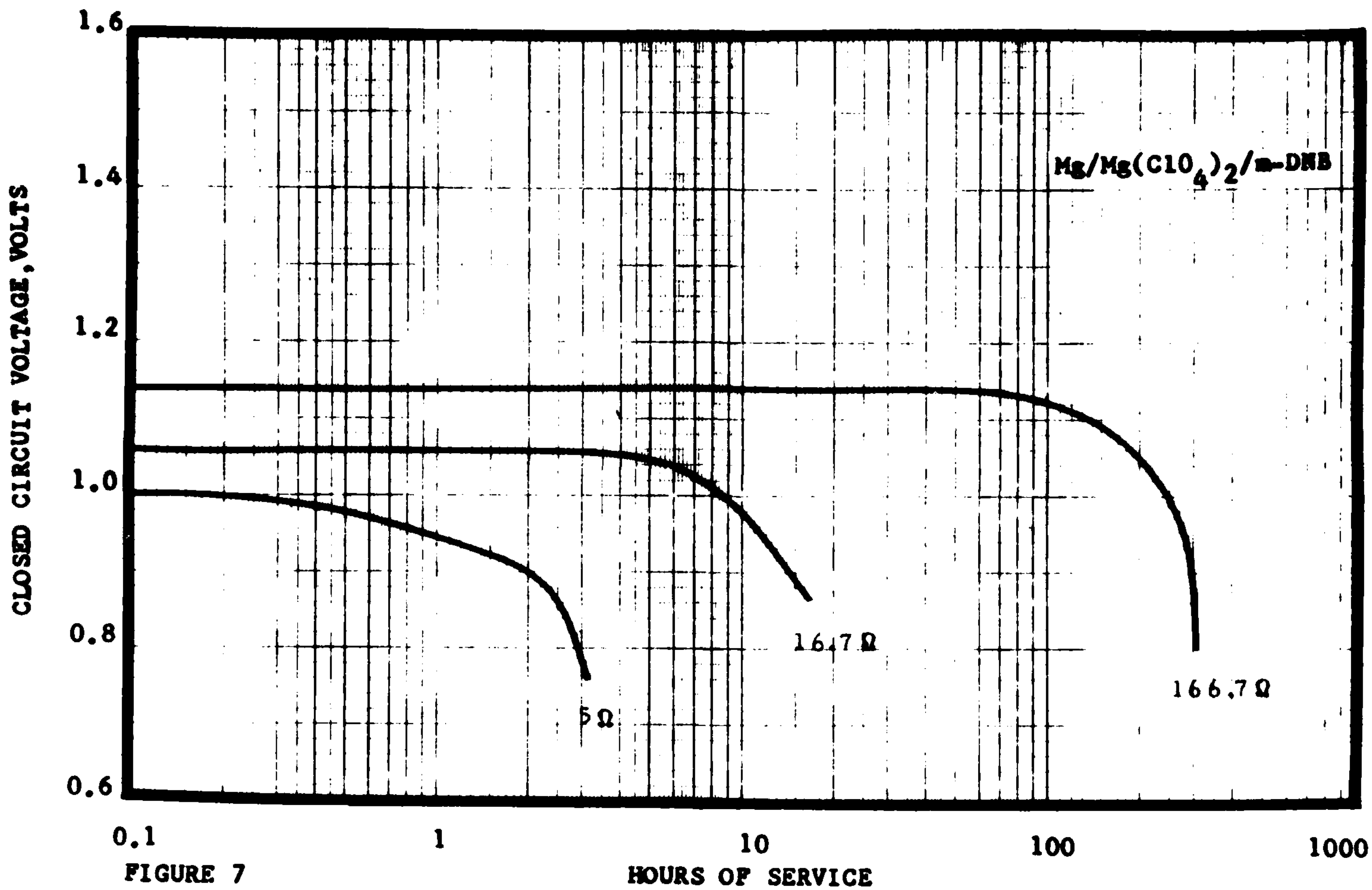


FIGURE 7

DISCHARGE CURVES AT 20°F FOR "A" CELLS

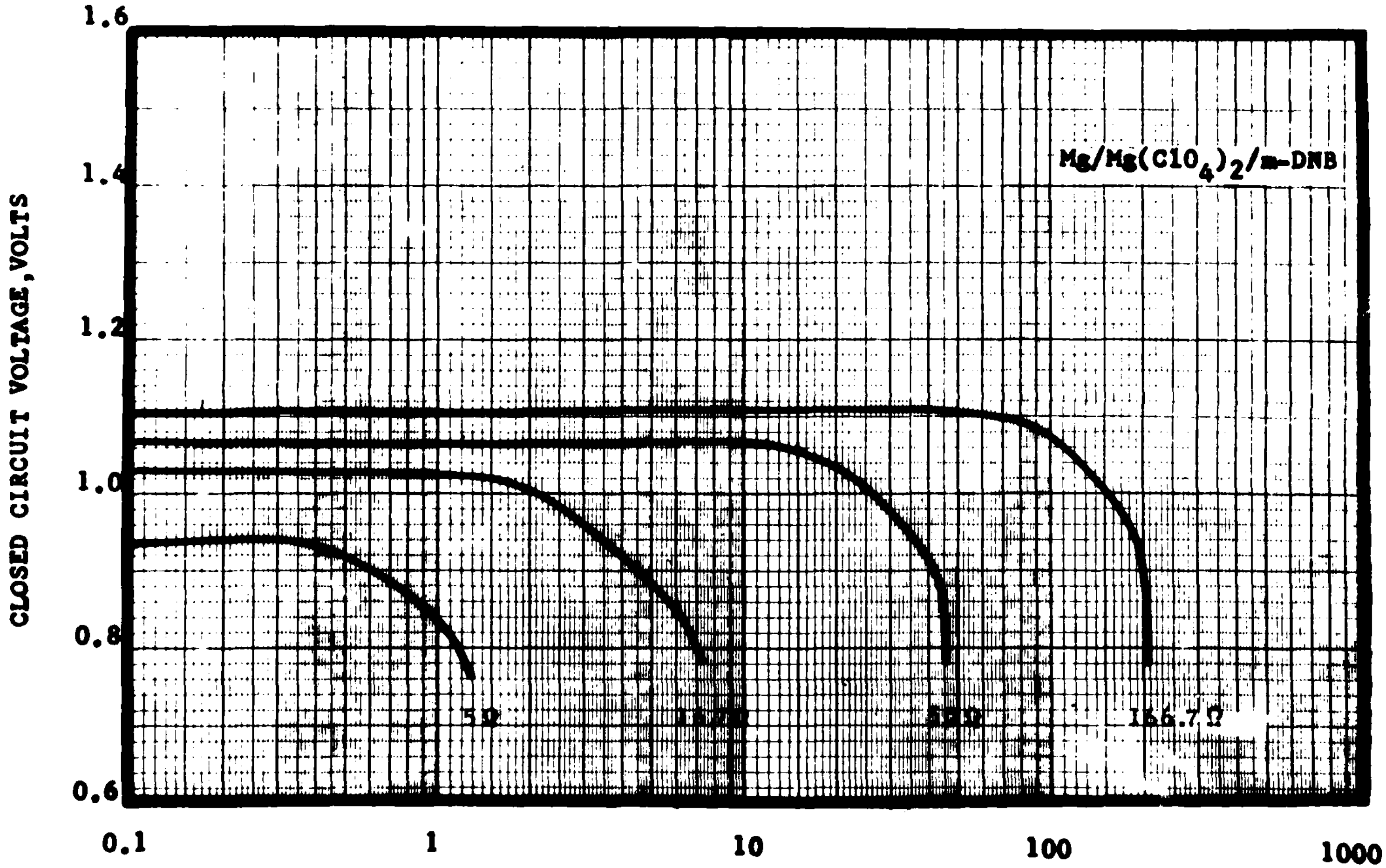


FIGURE 8

DISCHARGE CURVES AT 0°F FOR "A" CELLS

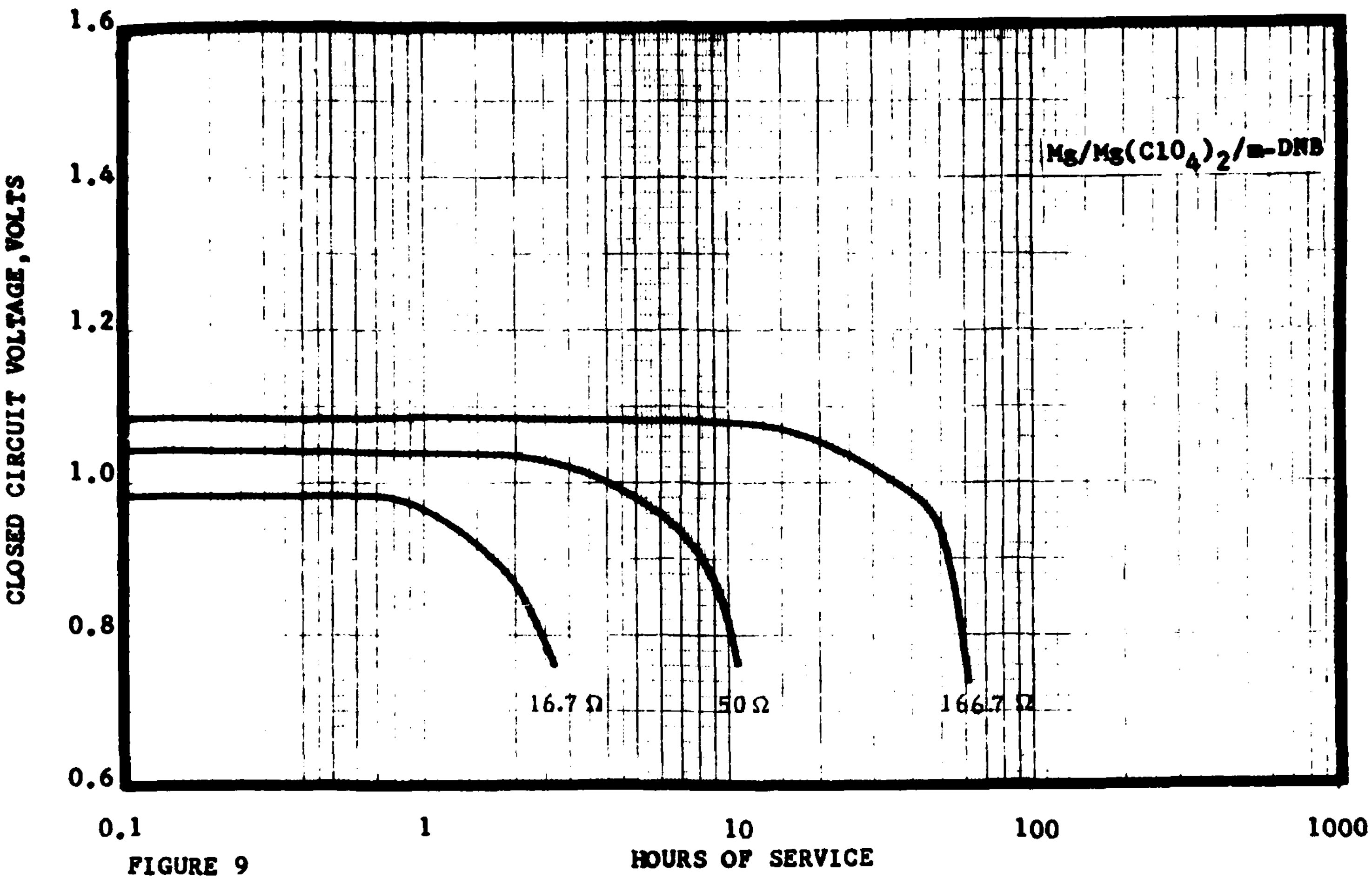


FIGURE 9

DISCHARGE CURVES AT 70°F FOR "D" CELLS

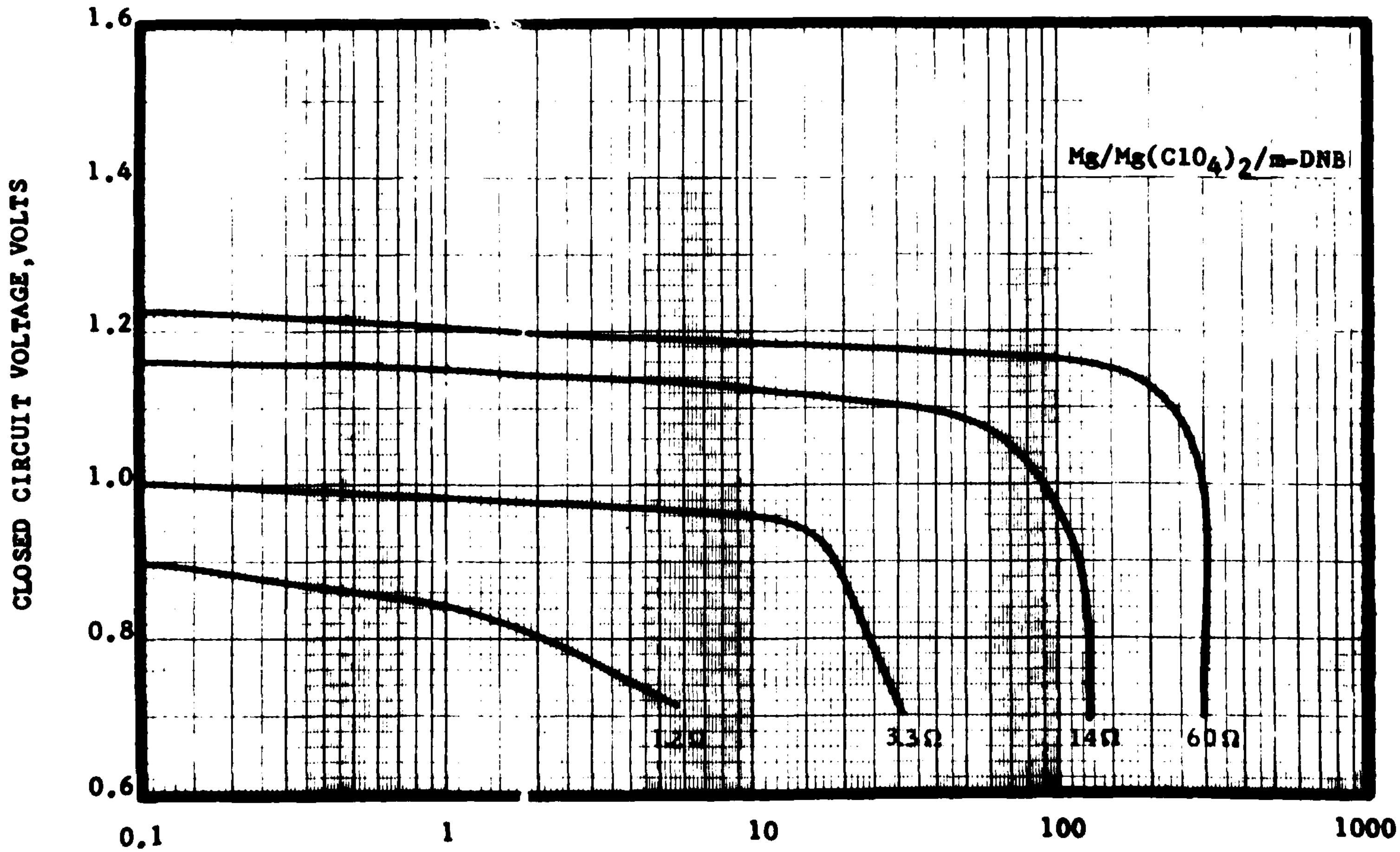


FIGURE 10

DISCHARGE CURVES AT 40°F FOR "D" CELLS

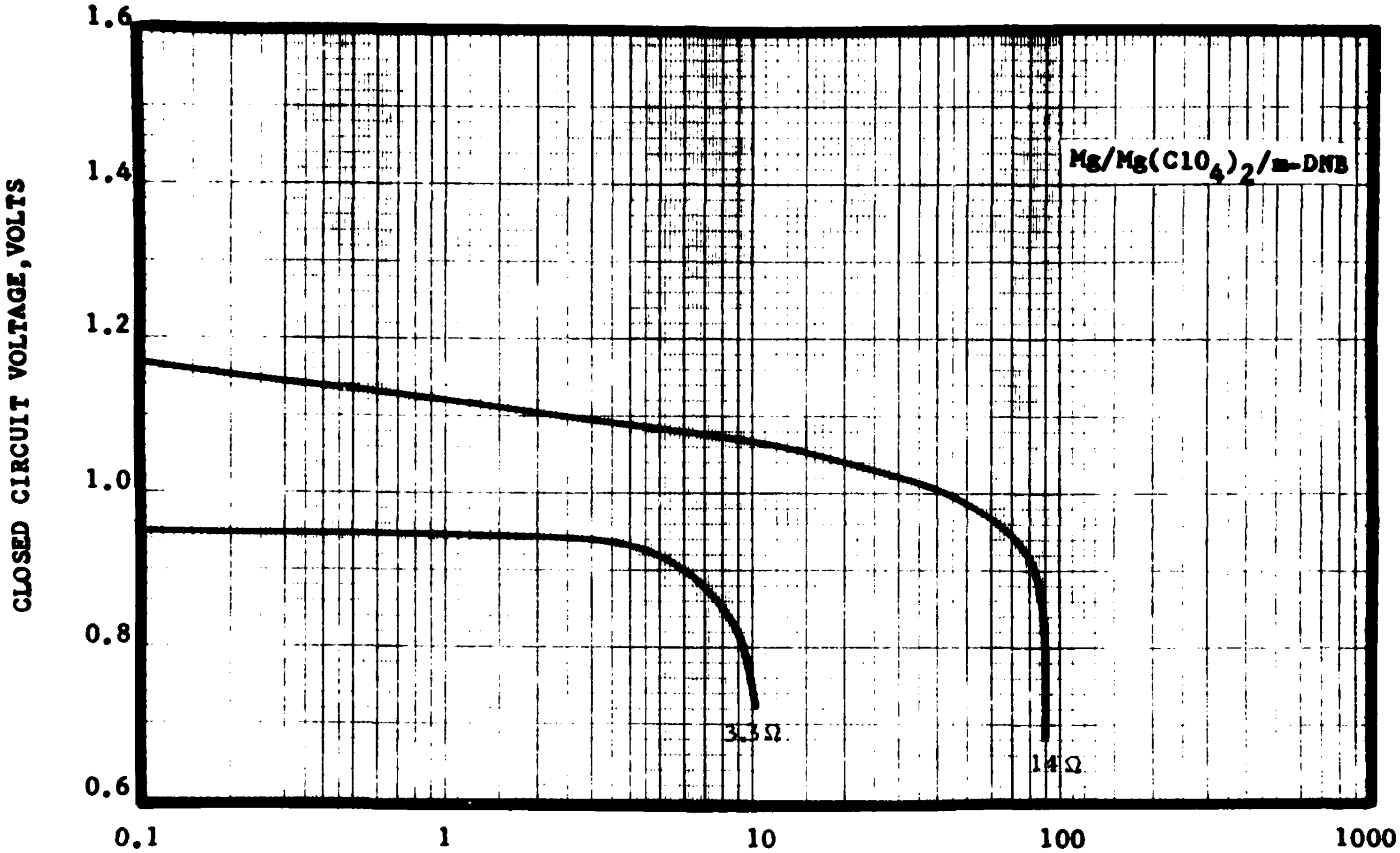


FIGURE 11

DISCHARGE CURVES AT 20°F FOR "D" CELLS

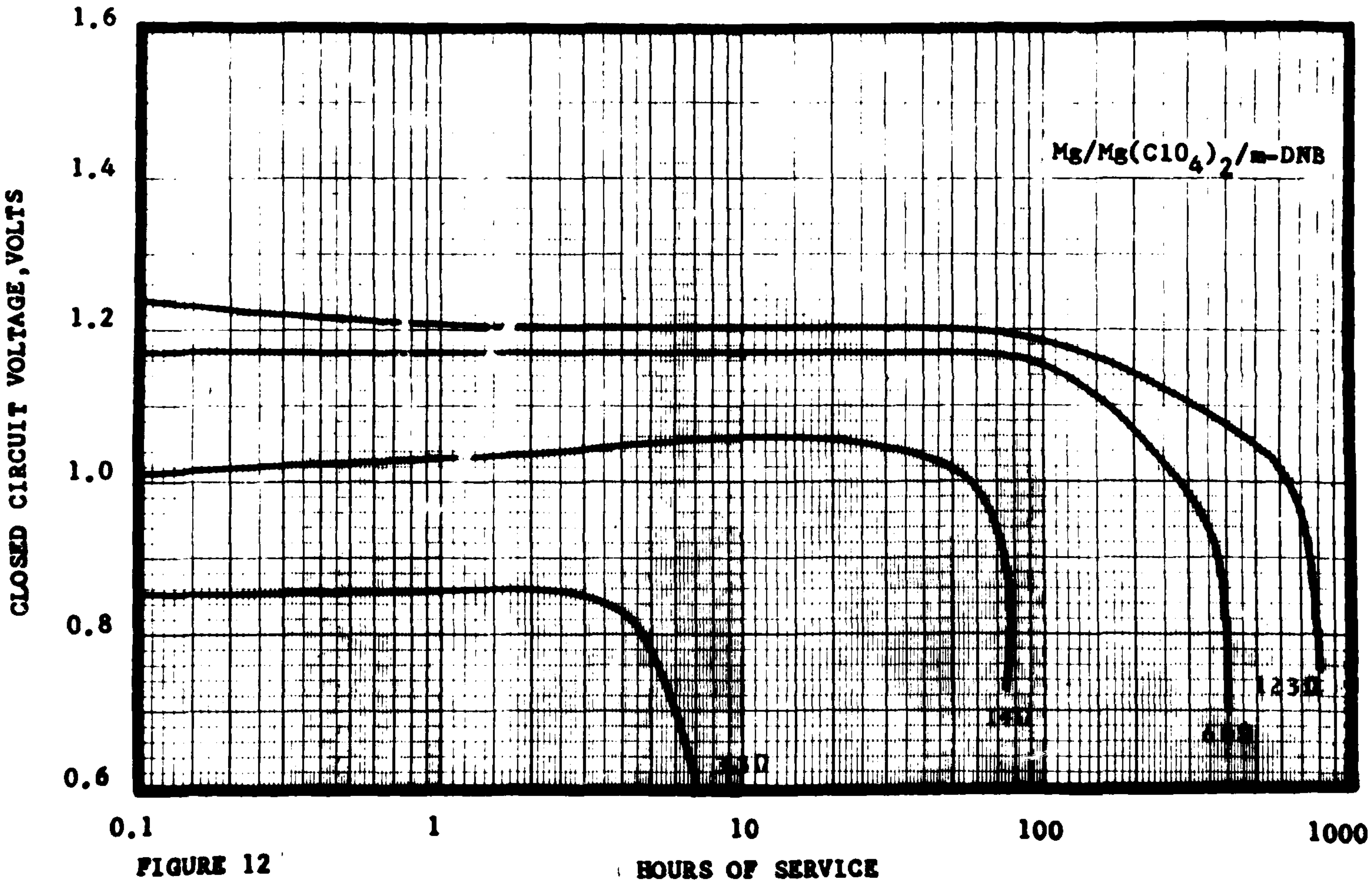


FIGURE 12

DISCHARGE CURVES AT $0^{o}F$ FOR "D" CELLS

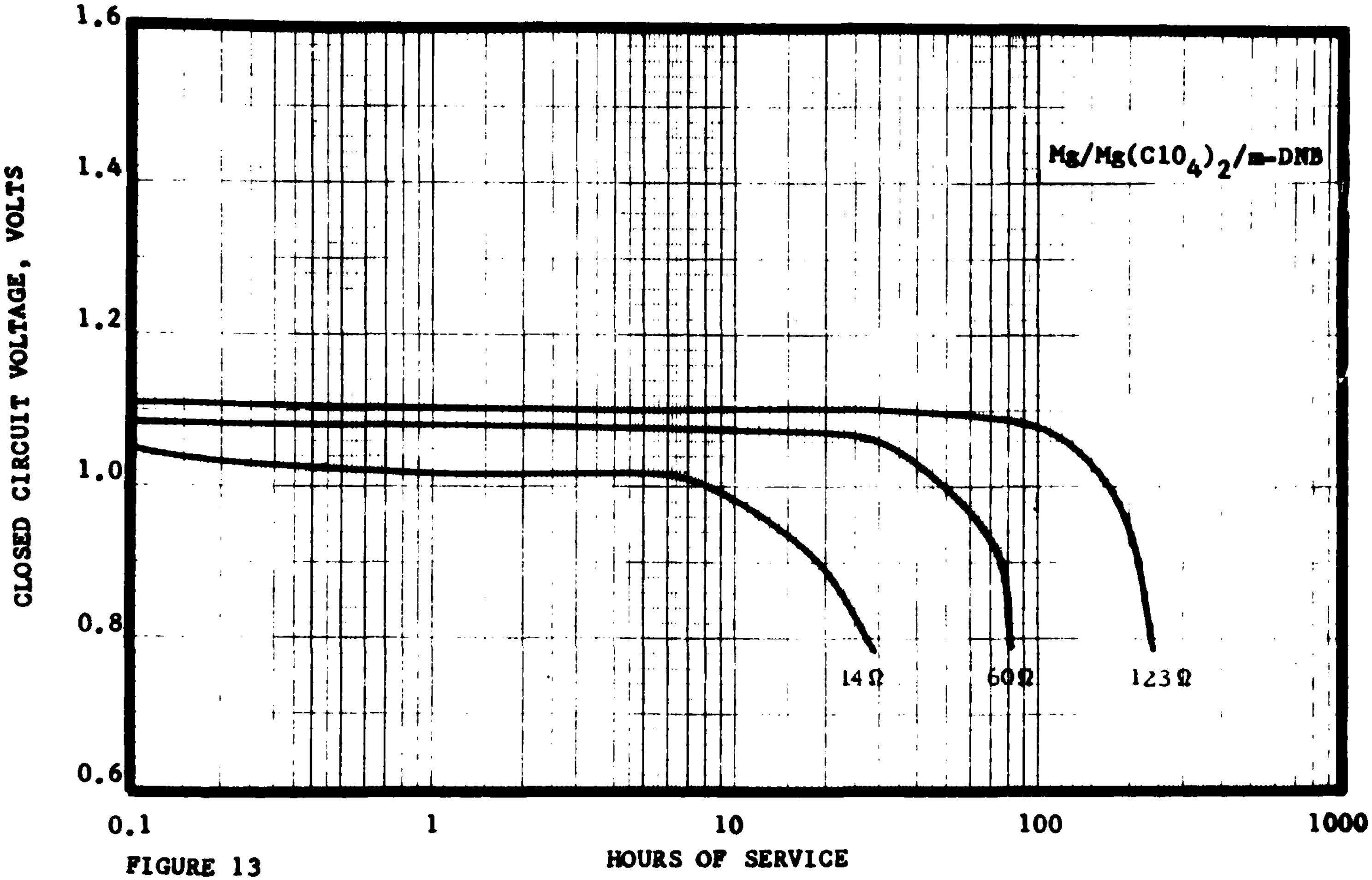


FIGURE 13

HOURS OF SERVICE AT VARIOUS TEMPERATURES

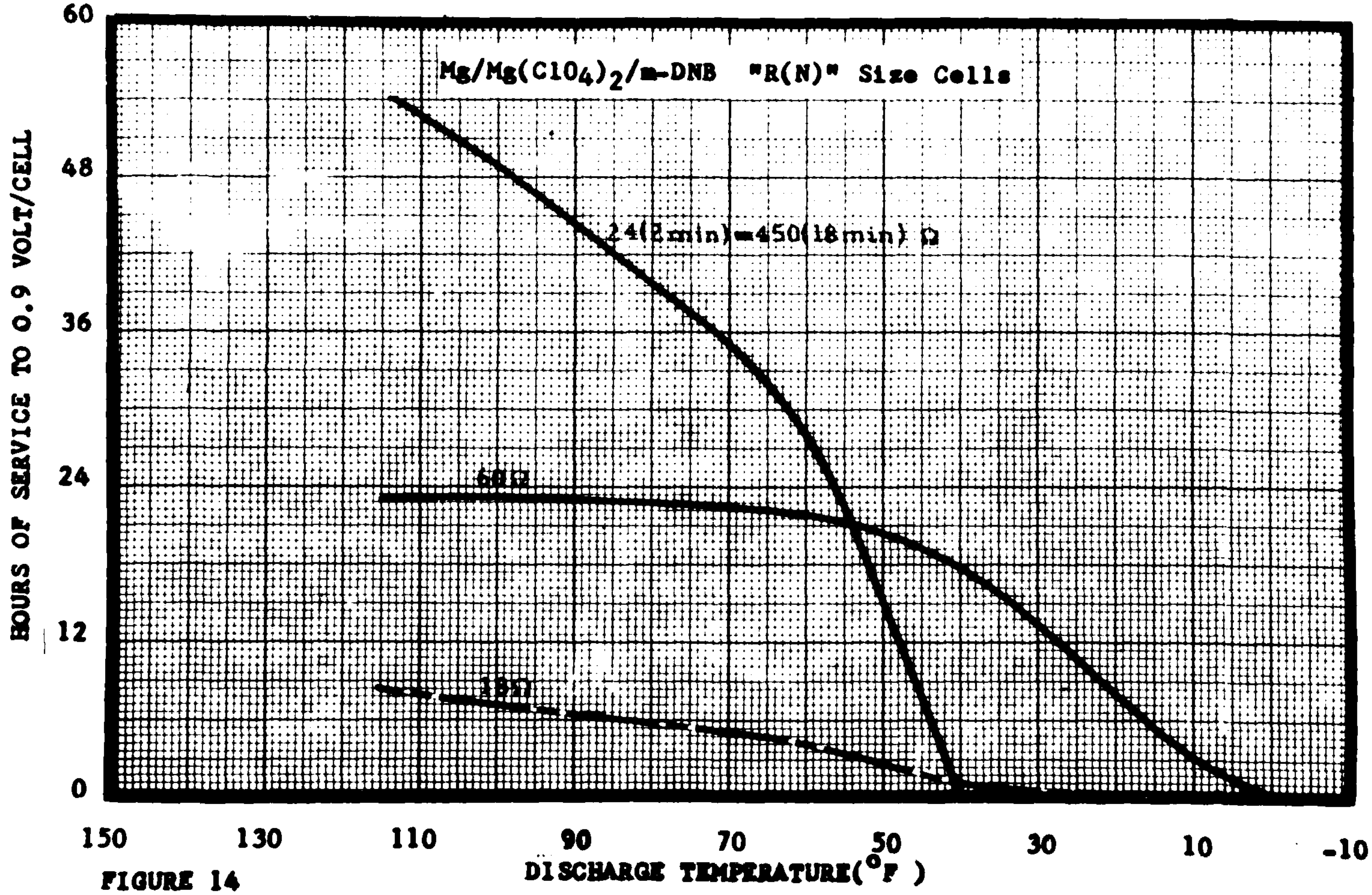


FIGURE 14

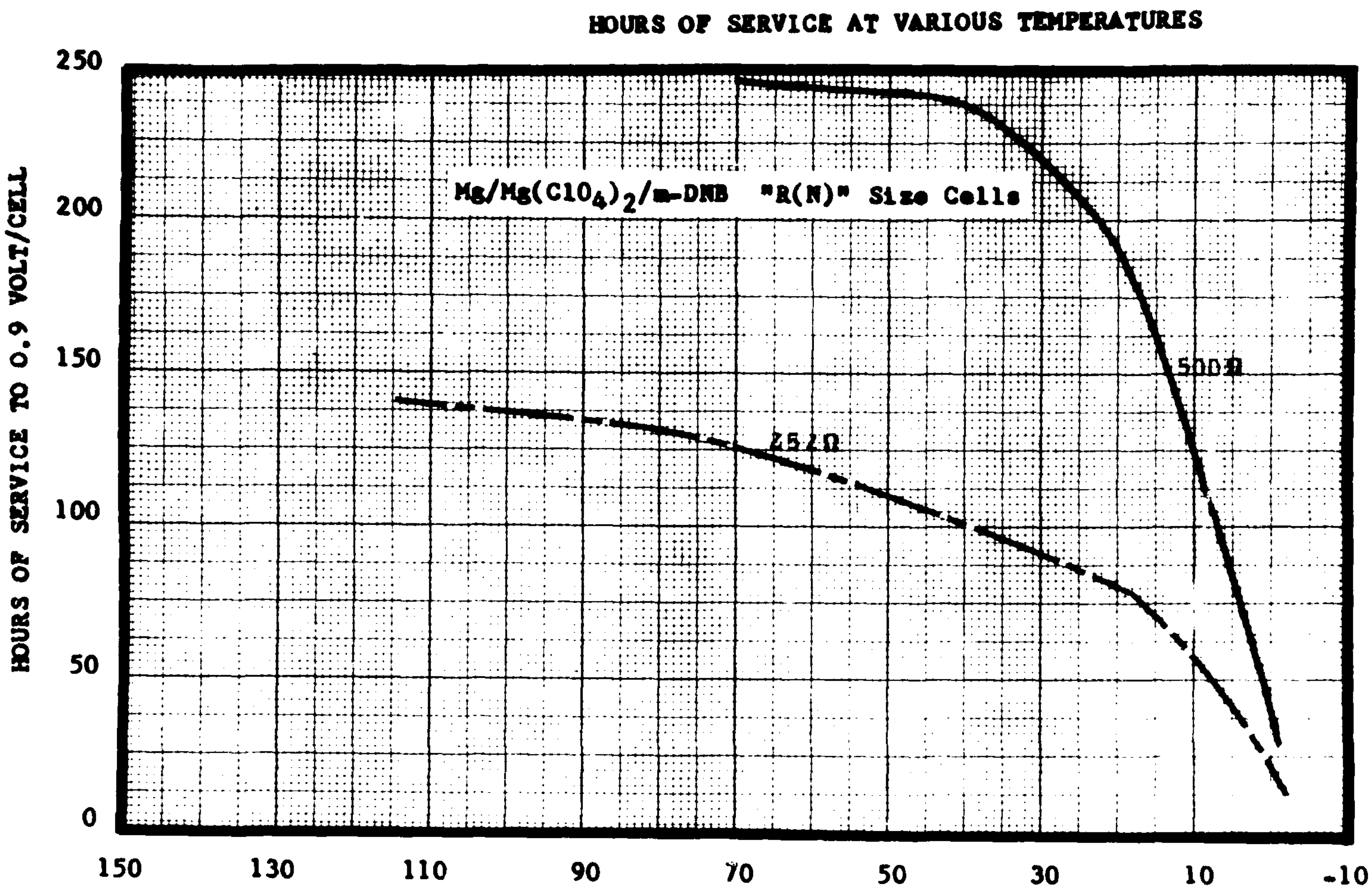
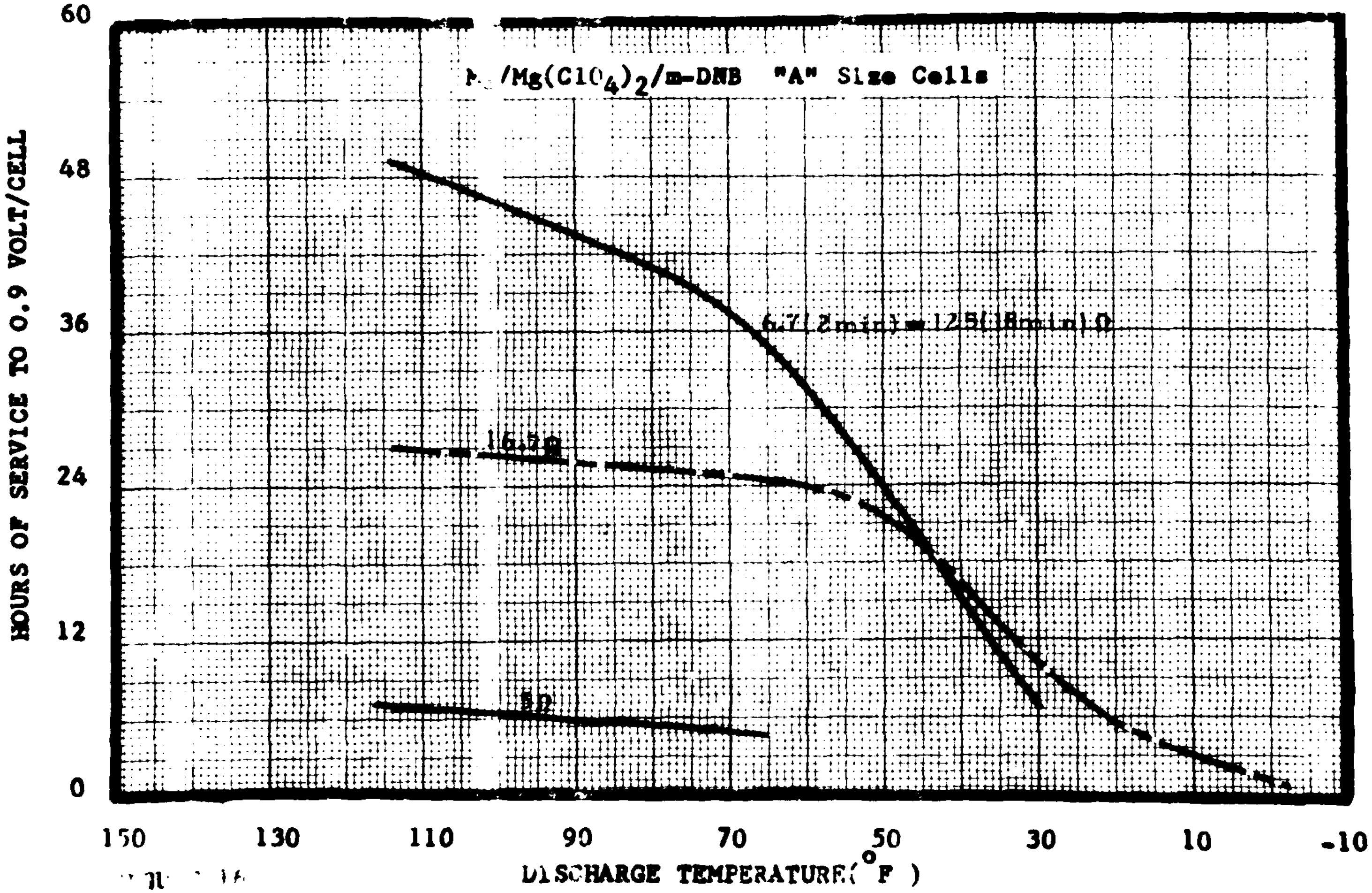


FIGURE 15

DISCHARGE TEMPERATURE(°F)

HOURS OF SERVICE AT VARIOUS TEMPERATURES



HOURS OF SERVICE AT VARIOUS TEMPERATURES

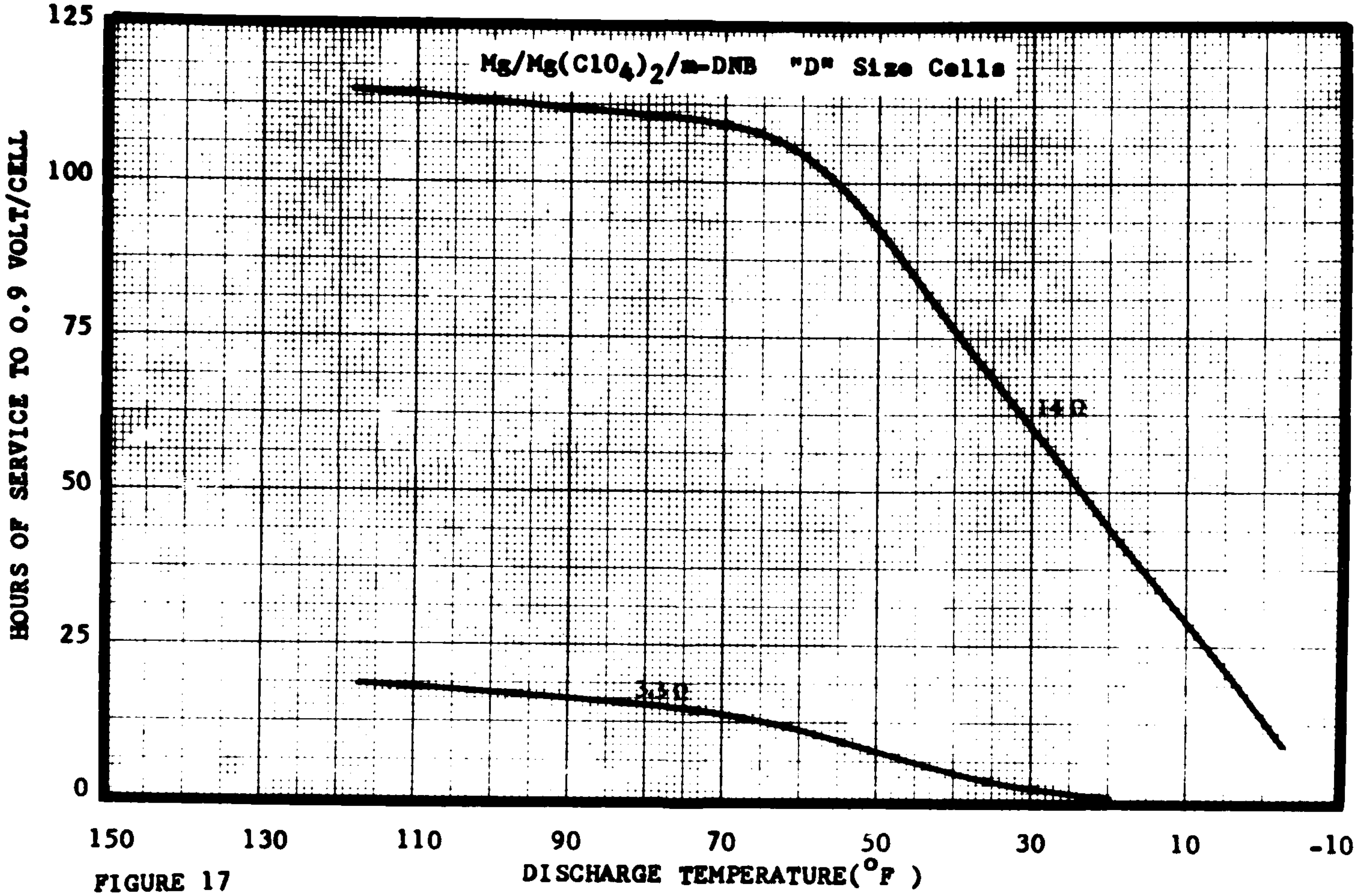


FIGURE 17

HOURS OF SERVICE AT VARIOUS TEMPERATURES

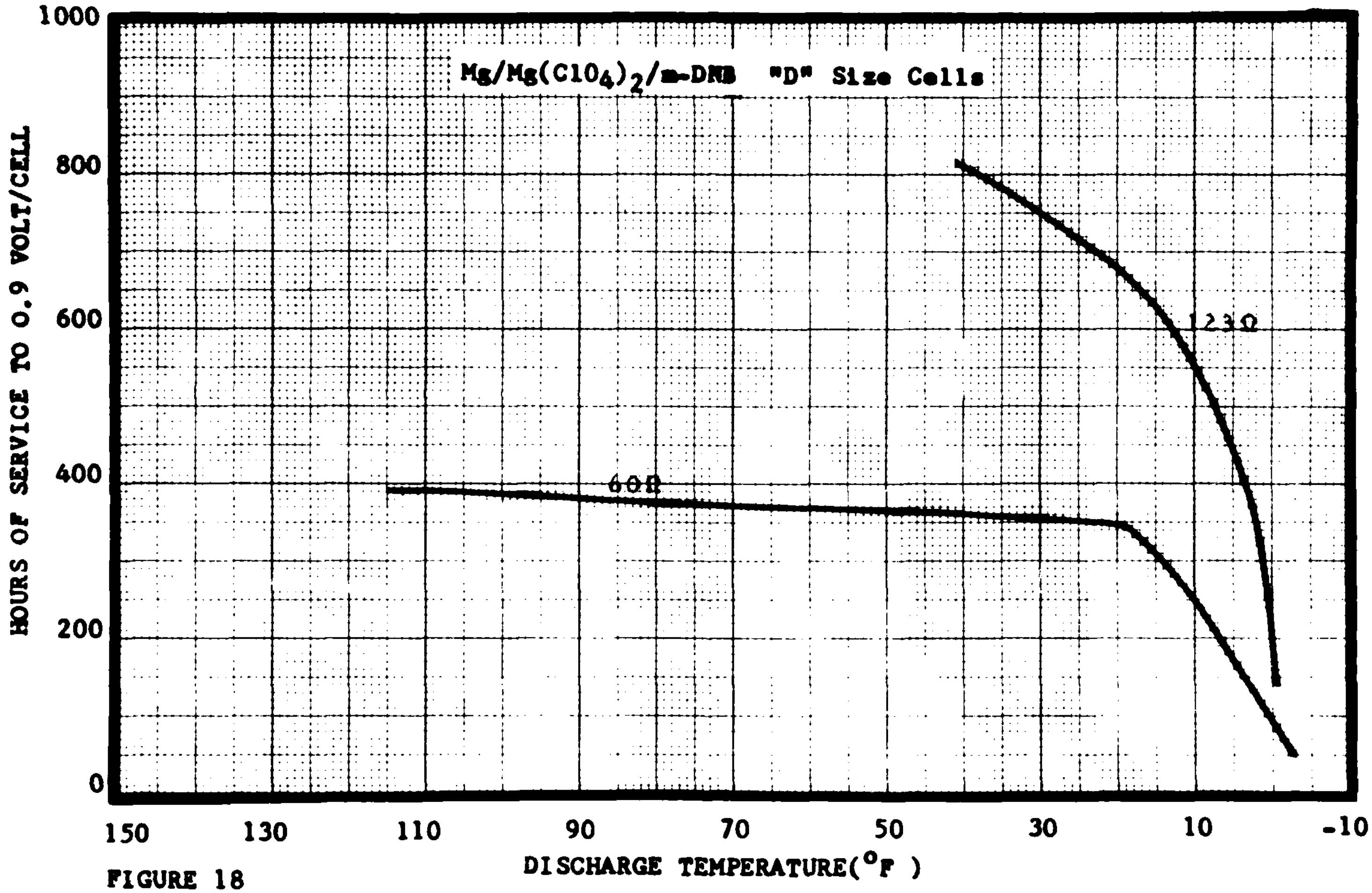


FIGURE 18

TABLE 3

SHELF-LIFE DATA FOR $Mg/Mg(ClO_4)_2$/m-DNB "R(N)" SIZE DRY CELLS

TEMPERATURE (°F.)	LOAD (Ohms)	STORAGE (Months)	HOURS OF SERVICE	% OF INITIAL CAPACITY RETAINED
70	18	Fresh	5.6	
70	"	3	4.7	83.9
70	"	6	4.2	74.9
70	"	12	3.7	66.2
113	"	3	4.1	73.3
113	"	6	2.0	35.7
70	60	Fresh	25.6	
70	"	3	22.3	87.1
70	"	12	20.7	80.9
113	"	3	19.0	74.3
113	"	6	17.3	67.6
130	"	3	17.3	67.6
130	"	6	11.4	44.5
70	252	Fresh	126.0	
70	"	6	120.0	95.4
70	"	12	102.9	81.6
113	"	3	109.0	86.5
113	"	6	105.5	83.9
113	"	12	59.1	46.8
70	24 Ohms (2 Min)	Fresh	36.4	
70	and 450 Ohms (18 Min)	12	17.7	48.6
113	"	3	29.8	81.9

TABLE 4

SHELF-LIFE DATA FOR $Mg/Mg(ClO_4)_2$/m-DNB "A" SIZE DRY CELLS

TEMPERATURE (°F.)	LOAD (Ohms)	STORAGE (Months)	HOURS OF SERVICE	% OF INITIAL CAPACITY RETAI
70	5	Fresh	5.6	
70	"	12	4.4	78.6
113	"	3	3.7	66.2
113	"	6	4.0	71.5
70	16-2/3	Fresh	25.6	
70	"	6	25.2	98.5
70	"	12	24.3	94.8
113	"	3	18.4	71.9
113	"	6	18.1	70.8
130	"	1	22.2	86.8
70	50	Fresh	94	
70	"	6	84	89.4
70	70	Fresh	129.9	
70	"	12	124.2	95.9
113	"	3	115.2	88.7
113	"	6	74.4	57.3
113	"	12	71.4	55.0
70	6-2/3 Ohms (2 Min)	Fresh	38.7	
70	and 125 Ohms (18 Min)	12	34.1	86.0
113	"	3	33.1	85.5
113	"	6	15.4	39.8

TABLE 5

SHELF-LIFE DATA FOR $Mg/Mg(ClO_4)_2$/m-DNB "D" SIZE DRY CELLS

TEMPERATURE (°F.)	LOAD (Ohms)	STORAGE (Months)	HOURS OF SERVICE	% OF INITIAL CAPACITY RETAI
70	3-1/3	Fresh	17.3	
70	"	3	15.6	90.2
70	"	12	15.4	89.0
113	"	3	14.5	83.8
113	"	6	10.7	61.8
113	"	12	7.8	45.1
70	14	Fresh	111.0	
70	"	12	107.2	96.8
113	"	3	107.1	96.5
113	"	6	91.6	82.6
113	"	12	82.7	74.5
130	"	3	97.3	87.6
130	"	12	76.5	68.8

It is believed that further refinements in sealing, such as a more reliable mechanical seal, should increase the capacity as a physical examination of stored cells revealed dryness in the cathode mix. The end-voltage for the useful service life was taken to be 0.9 volt/cell for the data presented in Tables 3, 4 and 5. Individual cell data from the groups analyzed in the tables implies that the system is stable at these temperatures (up to 130°F.) if the cell is manufactured in such a way to retain its moisture and vent hydrogen during discharge. The development of the mechanical seal has been accomplished in the $Mg/Mg(ClO_4)_2/MnO_2$ dry cell. It is essential that the $Mg/Mg(ClO_4)_2$/m-DNB dry cells be characterized in storage stability up to 160°F. as this is desired for most military applications in order to avoid the need for controlled storage conditions for dry batteries.

Even though some results for storage at 130°F. are indicated in Tables 3, 4 and 5, there was considerable evidence of magnesium can corrosion (pin-holing) for $Mg/Mg(ClO_4)_2$/m-DNB dry cells stored at this temperature, resulting in poor service life and inoperative dry cells. This type of corrosion was present even at 70°F. and 113°F. storage, but not to the extent which occurred at 130°F. The control of this corrosion aspect must be undertaken in order that the $Mg/Mg(ClO_4)_2$/m-DNB system be stable at high temperatures (130 to 160°F.).

SYSTEM COMPARISONS

Table 6 gives an indication of the watt-hours per pound and per cubic inch at 70°F. for the various cell sizes for the $Mg/Mg(ClO_4)_2$/m-DNB and $Mg/Mg(ClO_4)_2/MnO_2$ systems at the 25-and 100-hour rate.

TABLE 6

ENERGY DENSITY COMPARISONS BETWEEN
$Mg/Mg(ClO_4)_2$/m-DNB and $Mg/Mg(ClO_4)_2/MnO_2$
at the 25-and 100-Hour Rate

ELECTROCHEMICAL SYSTEM	CELL SIZE	HOURLY RATE	WATT-HR/LB	WATT-HR/IN^3
$Mg/Mg(ClO_4)_2$/m-DNB	R(N)	25	44.4	2.2
	A	25	58.2	2.9
	D	25	40.4	1.9
	R(N)	100	58.3	2.9
	A	100	76.0	3.8
	D	100	71.6	3.4
$Mg/Mg(ClO_4)_2/MnO_2$*	A	25	45.3	3.0
	D	25	36.2	2.1
	A	100	50.2	3.4
	D	100	52.5	3.1

* SYNTHETIC MnO_2

ALL CELLS TAKEN TO END-VOLTAGE OF 0.9 VOLT/CELL

The discharge curve data are the results of subjecting the cells to various resistances to obtain the desired rates and all data were obtained to an end-voltage of 0.9 volt/cell. From the data presented herein, it is apparent that there is little difference between the two systems at the 25-hour rate, but at the 100-hour rate the $Mg/Mg(ClO_4)_2$/m-DNB system is far superior to the $Mg/Mg(ClO_4)_2/MnO_2$ system based on watt-hours per pound. It is to be noted that the "A" size cell was found to give the best performance at the 25- and 100-hour rate for the $Mg/Mg(ClO_4)_2$/m-DNB system. There is little difference between the watt-hours per cubic inch data for the two systems. No valid comparisons could be made for the "R(N)" cell between the systems because of a lack of "R(N)" data for the $Mg/Mg(ClO_4)_2/MnO_2$ system.

In Figure 19, a comparison of discharge curves at 70°F. for "A" cells is given for the two magnesium systems. It is quite obvious that the Mg/MnO_2 system has a much higher discharge voltage, and its discharge curve is not as flat as the Mg/m-DNB system.

A comparison of service at various temperatures is given in Figure 20 and clearly illustrates that the Mg/m-DNB system gives poor service compared to Mg/MnO_2 at temperatures below 70°F. and only fairly comparable service to the Mg/MnO_2 system above 70°F.

A BA-4520( )/U Battery designed with 66 "A" size cells utilizing m-DNB would give at least 26 hours of service at 70°F as compared to 23 hours with the MnO_2 version of the battery unit. The Mg/MnO_2 battery weighs approximately 2.7 pounds and the Mg/m-DNB battery weighs 2.2 pounds. Both batteries have a volume of 62 cubic inches.

CONCLUSIONS

The Mg/m-DNB system has the following characteristics:

1. Operational voltage is approximately 1.0-1.2 volts per cell under a nominal load but a very flat discharge curve is typical.

2. Temperature dependence is reflected in decreased service life for temperatures below 70°F, and is greater than the present Mg/MnO_2 system.

3. Poor storage is evident at temperatures of 130°F or above. This is recognized to be a function of the wax seal used herein, and apparently uninhibited corrosion effects.

4. At 70°F, comparable watt-hours per pound are obtained for the Mg/m-DNB and the Mg/MnO_2 at the 25-hour rate. At the 100-hour rate, approximately 50% more watt-hours per pound are obtained with the Mg/m-DNB system.

COMPARISON OF DISCHARGE CURVES AT 70°F FOR "A" CELLS

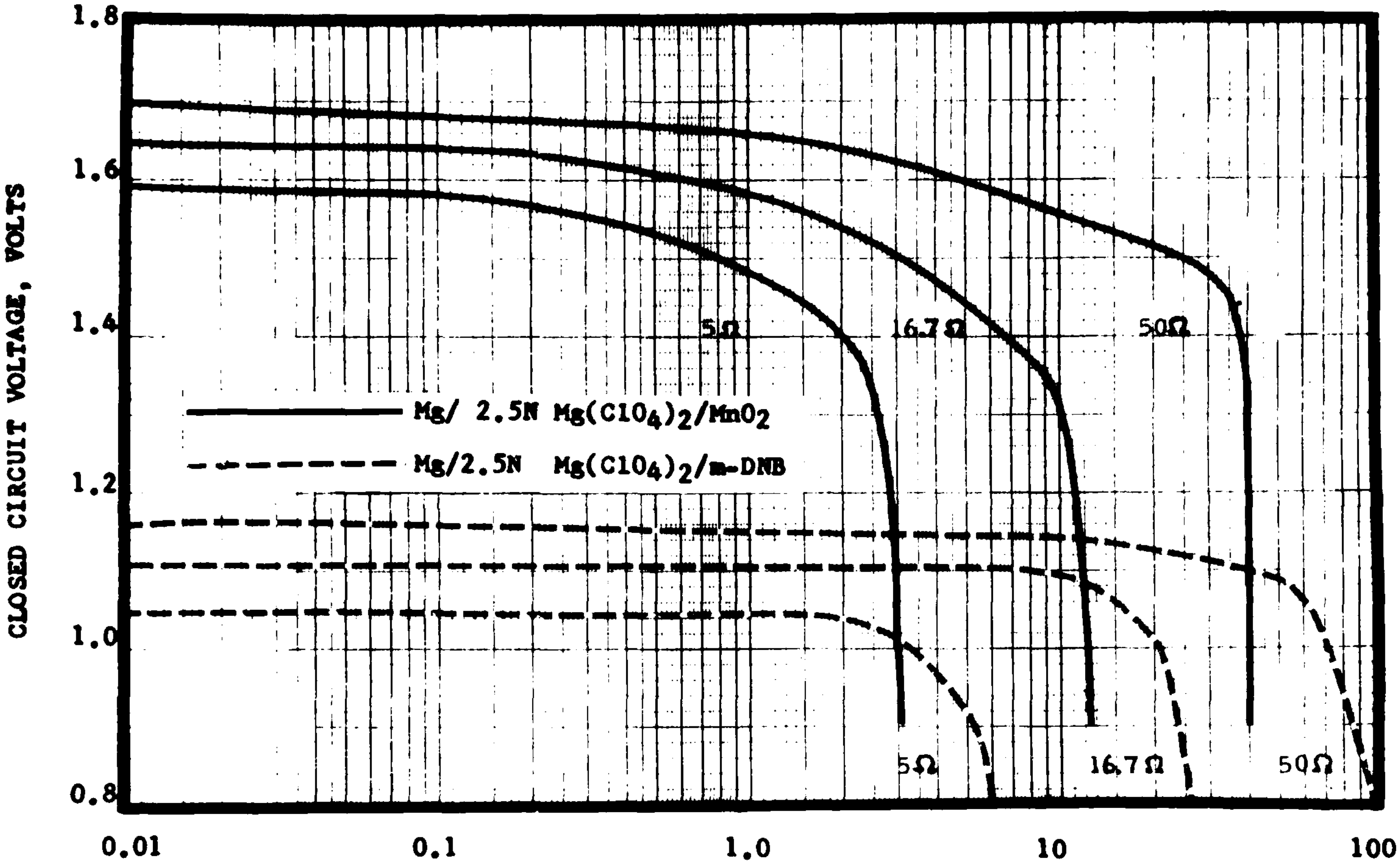


FIGURE 19

HOURS OF SERVICE

COMPARISON OF SERVICE AT VARIOUS TEMPERATURES

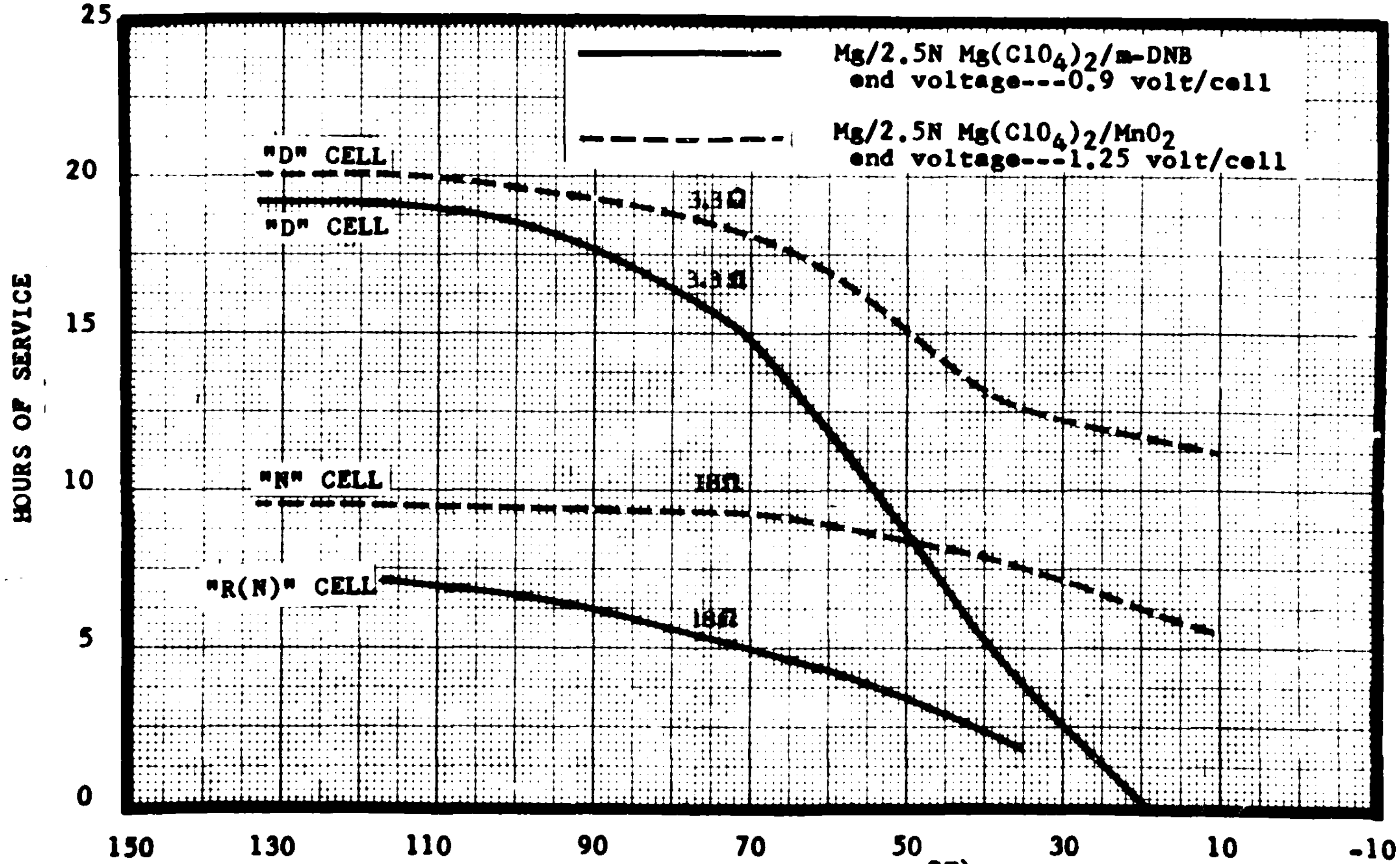


FIGURE 20

RECOMMENDATION

It is apparent that the Mg/m-DNB system requires improvement in the areas of cathode efficiency, corrosion inhibition and mechanical sealing. With the solution or alleviation of these factors, it is anticipated that the Mg/m-DNB system will show more promise and possibly compete with the Mg/MnO_2 system in various areas of utilization.

REFERENCES

1. Sol S. Jaffe, "Organic Depolarized Cells Utilizing Meta-Dinitrobenzene," Reports 1 through 5, 15 June 1965 to 15 November 1968, Contract DA28-043-AMC-01401(E) (USAECOM), Bright Star Industries, Inc.

2. J. C. Pawlak, "Organic Depolarized Primary Batteries," Technical Report ECOM-2753, July 1966 (Progress Report No. 2) (AD 616120).

3. J. C. Pawlak, "Organic Depolarized Primary Batteries," Technical Report ECOM-2567, March 1965 (Progress Report No. 1) (AD 638305).

4. J. J. Murphy and D. B. Wood, "Magnesium Battery Program," Proc. 21st Annual Power Sources Conference, 100 (1967).

5. J. B. Doe and D. B. Wood, "M-Dinitrobenzene Cell Performance," Proc. 22nd Annual Power Sources Conference, 97 (1968).

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13. ABSTRACT

The performance of the $Mg/Mg(ClO_4)_2$/m-DNB system is evaluated for various temperatures, hourly rates, and shelf-life periods. Extensive data is given for three cell sizes: "R(N)", "A" and "D". Techniques for fabrication of the above cells, which are adaptable for high-speed assembly, are mentioned. Finally, a comparison of the $Mg/Mg(ClO_4)_2$/m-DNB system with the $Mg/Mg(ClO_4)_2/MnO_2$ is given with respect to energy densities and performance curves. Improvements in cathode efficiency, corrosion inhibition, and a mechanical seal will have to be initiated in the Mg/m-DNB system before it will be able to compete with the present Mg/MnO_2 system.

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Security Classification

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Meta-dinitrobenzene (m-DNB)						
Magnesium dry battery						
Primary dry battery						
Magnesium - Organic dry battery						
$Mg/Mg(ClO_4)_2$/m-DNB						
$Mg/Mg(ClO_4)_2/MnO_2$						
ESC-FM - 1161 - 69						

Security Classification